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Tailoring of Narrow Pores, Pore Size Distribution and Structural Details in Asymmetric Nanofiltration Membranes via Polyvinyl-pyrrolidone Additive

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Abstract

The roles of polyvinyl-pyrrolidone (PVP) additive in the tailoring of pores, pore size distribution, morphologies and molecular weight cut-off (MWCO) in phase inversion asymmetric nanofiltration membranes was addressed. Using established solute transport method, scanning electron microscopy (SEM) and Minitab software, details analysis of the enhanced performance-properties of narrow pores nanofiltration membranes were verified. Experimental and analysis data revealed that the membranes prepared with 2 wt% of PVP demonstrated fine performance-properties. At this concentration, the fabricated nanofiltration membranes possessed narrow pore size and molecular weight cut-off of 1.14 nm and 2290 Da, respectively. In addition, the fabricated nanofiltration membranes displayed fine structural details of narrow pore size distribution, good morphology and critical key properties. With the combinations of thinner skin layer, fine structures and narrow pores, it can be concluded that the 2 wt% of PVP is the optimum PVP concentration to produce selective narrow pore nanofiltration membranes. Eventually, summary data on pores, pore size distributions (PSDs) and key properties proved that the PVP additive is effective for controlling performances-properties and structural details in asymmetrical based membranes.

Keywords

additive, molecular weight cut-off, morphology, nanofiltration, narrow pore, polyvinyl-pyrrolidone

1 Introduction

Polymeric based asymmetric membranes are mostly prepared by phase inversion process via immersion precipitation technique. Currently, fabricated membranes have been successfully used for different applications [1–6]. The phase inversion process involves the development of a thin active layer, membranes pores and structures in asymmetrical membranes as well as nanofiltration membranes [7]. In the nanofiltration process, the electrolytes are separated from aqueous solutions. The nanofiltration membrane is very efficient for separating solute (neutral or charged) and ionic compounds owing to the combination of steric (sieving) and electrostatic (Donnan) partition effects between membrane and external solutions [8, 9]. Membrane rejection differences can be used to regulate the single and multiple ions rejections [10].

1.1 PVP additives in membranes making

In the making of asymmetric membranes, the presence of polyvinyl-pyrrolidone (PVP) has been discovered to alter the formation of macro-voids linked to the instantaneous de-mixing mechanism [11]. This is due to the dope's thermodynamic instability in reaction with the non-solvent (water) that will increase due to the inclusion of PVP. Additionally, as the number of additives increases, the dope solution will be more resistant to deform, obstructing component dispersion during the membrane making process [12]. During the process, the polyvinyl-pyrrolidone is considered to be dissolved in coagulation media. Meanwhile, PVP-containing sites develop micro-pores. Apart from the production of micro-pores, it is commonly known that adding polyvinyl-pyrrolidone into the dope solution would enhance porosity and eliminate macro-void formation [13].

The inclusion of polyvinyl-pyrrolidone into dope solution can accelerate the generation of macro-voids in membranes, leading to a higher pure water flux [12, 14]. Low molecular weight (M_w) polyvinyl-pyrrolidone generates tiny pores and is simply leached from membranes. On the other

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hand, large M_w polyvinyl-pyrrolidone persists and controls the void formation [15]. The increments M_w additives lead to denser and wider pores, which reflect lower separation efficacy and diverse pores [16]. The inhibition of macropores is also caused by the presence of a high concentration of PVP [17]. Previous studies demonstrated the ability of PVP as an efficient permeation flux agent since thermodynamics is critical during membrane development [18, 19].

1.2 Morphology and pores characteristics

The measurement of pores, shape and skin layer thickness determines the membrane capability and efficacy [20]. A low molecular weight component is frequently utilised as an additive in membrane formation systems. This kind of additive can manage the structure of the membrane using a practical technique of creating high-performance membranes [21–23].

Membrane separation capacities are strongly dependent on membrane structural parameters. A good understanding of structural characteristics is critical for controlling the quality and characteristics of membranes. The morphology of the skin layer determines the flux and rejection of membranes [24], good mechanical strength and membranes durability and industrial applicability [25].

Scanning electron microscopy (SEM) is a well-established membrane characterisation technique to examine the morphological structure of a membrane. As a result, good morphological structure determines the main goals of any process or technique used to fabricate membranes [26]. The influence of PVP additive on the morphology of asymmetric membranes has been explored by Han and Nam [27]. During the formation process, it is difficult to control the membranes and their performance. The membrane structure and performance mostly rely on several factors namely polymer, solvents and non-solvents, composition, coagulant types, and casting or spinning process. Since these factors are interdependent, changing one or more parameters results in a significant impact on membranes performance and properties [28, 29].

In membrane characterisation, the pores characteristics in asymmetrical membranes are commonly measured by using several techniques [30]. The major ones are:

1. Bubble pressure breakthrough: The pressurised air blown through a sample (liquid-filled) is to be measured in this approach.
2. Mercury porosimeter: This approach fills a dry membrane with mercury (a non-wetting fluid) employing the higher pressure and similar concepts as bubble pressure.
3. Electron microscopy: Scanning electron microscopy (SEM), transmission electron microscope (TEM) and scanning transmission electron microscope (STEM) microscopy techniques are used to observe the top and bottom of a cross-section of membranes.
4. Atomic force microscopy (AFM): This is a cutting-edge method for solid-state material surface analysis.
5. Solute transport method: This technique is based on the experimental test separation performances of macro-solutes/neutral solutes with different molecular weights.
6. Adsorption-desorption methods: This technique employs vapour pressure measurement based on the Kelvin equation.
7. Thermo-porometry: A differential scanning calorimeter, the pore size distribution (PSD) could be studied and phase change will be visualised (Differential scanning calorimetry, DSC).
8. Perm-porometry: This method uses the gas flux measurement over samples and the controlled blockage of pores by condensation of vapour presenting as a component of a gas mixture.
9. Nuclear magnetic resonance (NMR): The materials with a known pore population are used to calibrate the NMR measurement.

For the experimental and modelling prediction of molecular weight cut-off (MWCO), the poly(ethylene glycol) (PEG) solutes at different molecular weight are frequently used for membranes performance test [31]. This is due to their colloidal characteristics, which are only mildly affected by the chemical environment, resulting in minimal fouling levels [32]. Meanwhile, for membrane pore size distributions, a new technique called a fractional rejection of non-ionic and charged macromolecules is employed [33]. The solute transport method is used to establish the mean pore size, whereas the log-normal distribution is used to generate the pore size distribution [34].

The aims of this work are to study the effects of PVP additives and to produce low-pressure nanofiltration membranes. Using the established solute transport method, the characteristics of pores, pore size distribution and MWCO were determined. Significantly, this study discovered key properties of nanofiltration membranes that are critical technical properties for membranes-industrial application matching. Eventually, this study is very important for a simple technique of membrane performance-properties modification and accelerating the development of various low-pressure selective narrow pore membranes for different industrial application in future.

1.3 Theoretical background

1.3.1 Pore Size and Pore Size Distribution (PSD)

The sizes of pores, which are cross-sectionally changing channels, are referred to pore size of membranes. In geometries, the pore size is defined as the distance between two opposing pore walls. To achieve a good mean pore size, some averaging is done if the pores are unevenly formed with the assumption of a spherical equivalent. However, other representations have been proposed, such as cage-like/spherical mesoporous structures and non-spherical particles [35]. Several researchers reported that the mean pore sizes for high performance nanofiltration membranes are in the ranges of 0.3–1.5 nm as well as a good correlation between pore size distribution and narrow MWCO [36, 37].

Pore size determination and pore size distribution studies have been carried out using a variety of approaches such as SEM, AFM and retention of multi-dispersed solutes [38]. The scanning electron microscope is the simplest and most direct technique for morphological analysis. The result, however, is unreliable since heavy metals coated on membrane samples during the coating process may cause surface imperfections. Therefore, the solute transport method is commonly used for pore size and pore size distribution measurement. Filtration experiments using aqueous solutions of various solutes are used to develop the technique [39].

Solute Transport Method

Solute transport and gas permeation techniques are used to calculate the pore size for the pores open to flux, which are then linked to permeation parameters [40]. These two methods are crucial for characterising the thin layer in asymmetric membranes but provide little data about pores and pores size.

While measuring membrane rejection and modelling solute transport pathways, pore size is a crucial factor to be considered. In common practice, the pore size of membrane is determined by the MWCO. The size exclusion effect or a solute of concern can be measured by comparing the MWCO [41]. Solutes diffusivity in the solution is used to calculate its Stokes radius by using Eq. (1) [33]:

$$D_s = \frac{kT}{6 r_s \pi \mu}. \tag{1}$$

Log-normal probability function

The pore size distribution is commonly analysed by functional graph. The data of real permeation coefficients vs molecular weight plots and the permeation of solute solution are used in the analysis. The pore size distribution of the membrane can be identified from the probability density function with a log-normal distribution. The log-normal model may be changed by considering the link between molecular weight and molecule diameter, and it is a critical component in the explanation of organic molecule penetration [33, 39].

Based on the log-normal probability function, the relationship between separation efficacy and solute diameter can be written as:

$$R(\%) = erf(z) = \frac{1}{\sqrt{2\pi}} \int_{-\alpha}^{z} e - \frac{u^2}{2} du, \tag{2}$$

where:

$$z = \frac{\ln r_s - \ln \mu_s}{\ln \sigma_g}. \tag{3}$$

A straight line is obtained when the membrane's solute rejection is plotted against the solute radius on the log-normal probability coordinate as:

$$F\left(\mathrm{R}_{\mathrm{real}}\right) = A_0 + A_1 \left(\ln ds\right). \tag{4}$$

The r_s and M_w were determined based on the following relationship [33]:

$$\log r_s = -1.4853 + 0.461 \log M_w. \tag{5}$$

The PSD of the membrane could be described using the probability graph, which is solute separation data [34, 42].

$$\frac{df(r_p)}{dr_p} = \frac{1}{r_p \ln \sigma_p \sqrt{2\pi}} exp - \left[\frac{\left(\ln r_p - \ln \mu_p\right)^2}{2\left(\ln \sigma_p\right)^2} \right] \tag{6}$$

The approach has been used to calculate the mean pore size, pore size distribution, and membrane porosity.

1.3.2 Separation characteristics

The separation performance of the NF membranes be characterised by $\mathrm{R}_{\mathrm{real}}$ and $\mathrm{R}_{\mathrm{obs}}$ using Eqs. (7) and (8) [43, 44].

$$\mathrm{R}_{\mathrm{obs}} = \left[1 - \frac{C_p}{C_b}\right] \tag{7}$$

$$\mathrm{R}_{\mathrm{real}} = \left[1 - \frac{C_p}{C_w}\right] \times 100 \tag{8}$$

2 Materials and method

2.1 Chemicals

Polyethersulfonem (PES) from Amoco, N-methyl-2-pyrrolidone and polyvinyl-pyrrolidone (Merck) were used as polymer, solvent and additive, respectively. Methanol (Sigma Aldrich), water and distilled water were used as a post-treatment medium, coagulation bath and non-solvent, respectively. Neutral solutes with different series of M_W were used for solute separation test [22].

2.2 Dope formulations

To develop membranes formulations, different ternary/multi-component systems comprising polymer/solvent/non-solvent start with a turbidimetric titration process. This method is very important to obtain the homogenous and right compositions for each material in the multi-component dope solutions [45, 46]. In this step, 100 g of dope was titrated with water until the cloud state was reached. The clear polymer dope turned milky at this point. Then, the volume of water titrated was calculated and used in the real formulation.

In this study, a polymer concentration of 20.42 wt% was used to make a membrane dope solution. At temperature of 343.15 K, PES was dissolved in a multi-component system. During the process, different concentrations of PVP additives ranging from 2 wt% to 10 wt% were added to the solutions to produce five different formulations. Then, the prepared solutions were placed in an ultrasonic bath to eliminate air bubbles.

2.3 Casting dope and preparation of nanofilter

Using the phase inversion immersion precipitation technique, a thin flat sheet of nanofiltration (NF) membranes was cast at room temperature through the water as coagulant media for 24 hours. Then, the membranes were transferred into methanol for another 24 hours followed by a drying process.

2.4 Nanofiltration separation test and morphologies

Firstly, the nanofiltration membranes samples underwent a compression test (500 kPa) for 1 hour. The 20 mL of permeate flux was collected for analysis. The permeate was collected and weighed for every minute by an electronic balance. All the data are average values from three times of experimental works.

Using a dead-end filtration cell (Model Millipore) and membrane area of 1.39×10^{-3} m^2, the solute separations were measured in terms of solutes flux and real rejection at 500 kPa. The membrane separation performance was characterised in terms of real rejection, R_{real} and observed rejection, R_{obs}. In this analysis, the concentrations of neutral solutes were measured using a Total Organic Carbon analyzer (Thermo Scientific) while the membrane morphologies were analysed using SEM from JEOL JSM 6360LA, Japan.

3 Results and discussion

3.1 Narrow pores and pore size distribution

Fig. 1 depicts the Minitab log-normal probability graph of Stokes radius and solute rejection. Based on solutes of different M_w, the graph showed linear relationships with good correlations. Table 1 summarises the experimental data of flux, rejection and modelling data of mean pore radius (μ_p), and geometric standard deviation (σ_p).

The increase in PVP concentration caused the increase in mean pore radius and geometric standard deviation. In comparison, the addition of the PVP also affected the gradual increase in pore radius, geometric standard deviation and MWCO.

At the optimum condition (2 wt%), the fabricated narrow pore nanofiltration membrane was found to have of μ_p = 1.14 nm, σ_p = 1.66 and MWCO = 2290 Da. The increasing membrane pore radius and MWCO in the PVP additive were very useful as a pore former agent for asymmetrical polymeric membranes.

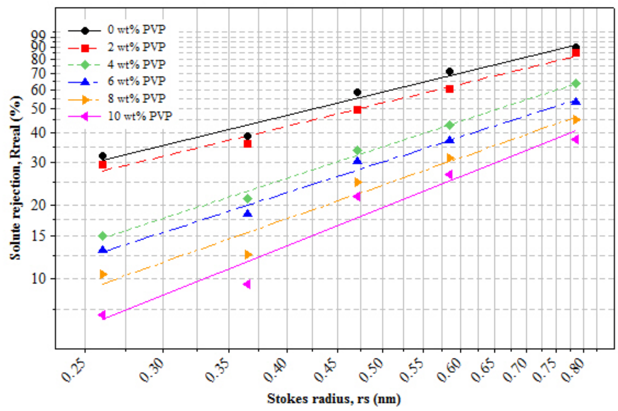

Fig. 1 Log-normal probability graph of NF membranes

Table 1 Flux, rejection, pores and MWCO of NF membranes

Membranes	J_v [a] ($\times 10^{-6}$ m^3/m^{2}s)	R_{real} [b] (%)	μ_p (nm)	σ_p (-)	MWCO (Da)
PVP 0 wt%	3.26	43.10	1.02	1.70	1905
PVP 2 wt%	3.61	46.94	1.14	1.66	2290
PVP 4 wt%	3.56	44.71	1.56	0.98	3932
PVP 6 wt%	3.14	43.22	1.79	1.00	5498
PVP 8 wt%	3.16	43.26	2.04	0.99	7174
PVP 10 wt%	3.04	44.09	2.34	0.99	9630

[a,b] are the flux and rejection data from [22]

Meanwhile, at higher PVP concentrations (> 6 wt%), the fabricated NF membranes exhibited higher pore radius and MWCO in the range of 1.79 nm to 2.34 nm and 5498 Da to 9630 Da, respectively. At lower concentrations (2–4 wt%), the PVP additive was significantly improved the membrane characteristics. As shown in Fig. 2, the nanofiltration membranes fabricated with 0 wt% and 2 wt% demonstrated narrow pore size distribution. However, better pore size distribution was shown by the membranes with 2 wt% of PVP. These results verified the experimental findings of enhanced fluxes and separation performance [16, 22].

3.2 Morphological structures

Fig. 3 displays the morphologies of fabricated nanofiltration membranes. Generally, the resultant membranes consisted of a thin skin layer and finger-like structures. A small amount of PVP produced the narrow pore nanofiltration membranes with a very thin skin layer, smaller finger-like structures and a smaller pore radius.

At 2 wt%, the membranes produced smaller, fine finger-like structures and micro-voids beneath the sub-layer compared to the membrane without PVP. Similar membrane morphology was also shown by 4 wt% of PVP membrane. The large numbers of fine finger-like pores and the existence of micro-voids in the 2 wt% and 4 wt% membranes resulted in better performance compared to the other membranes. Besides, at the optimum PVP concentration, the membrane active layer was reduced [27].

However, beyond the optimal point, the number of finger-like pores was found to be reduced. As the fine pore structures deteriorated, the skin layer thickness and pore radius increased. However, micro-voids were formed since increasing the PVP concentrations was not associated with a higher volume flux.

Meanwhile, at high PVP concentrations of 8 wt% to 10 wt%, the thicker skin layer thickness caused lower volume fluxes. Besides, a larger pore radius and macro-voids contributed to a fair salt rejection rate. At the highest PVP concentration of 10 wt%, the macro-voids structures are grown to the largest size due to the suppression of finger-like structures and promoted the formation of micro- and macro-voids beneath the sub-layer [47–49].

Therefore, considering the overall performances-properties, structural parameters morphologies, pores and PSDs, it can be concluded that the optimum PVP concentration was found at 2 wt% and the PVP additive played important roles and good material for controlling pores and morphological in asymmetrical based NF membranes as presented in Fig. 4.

4 Conclusions

Analysis data on the fabricated narrow pores nanofiltration membranes proved that the polyvinyl-pyrrolidone additives can enhance the characteristics of the NF membranes. Experimental data revealed that the optimum PVP concentration was found to be at 2 wt%. At this optimum point, the

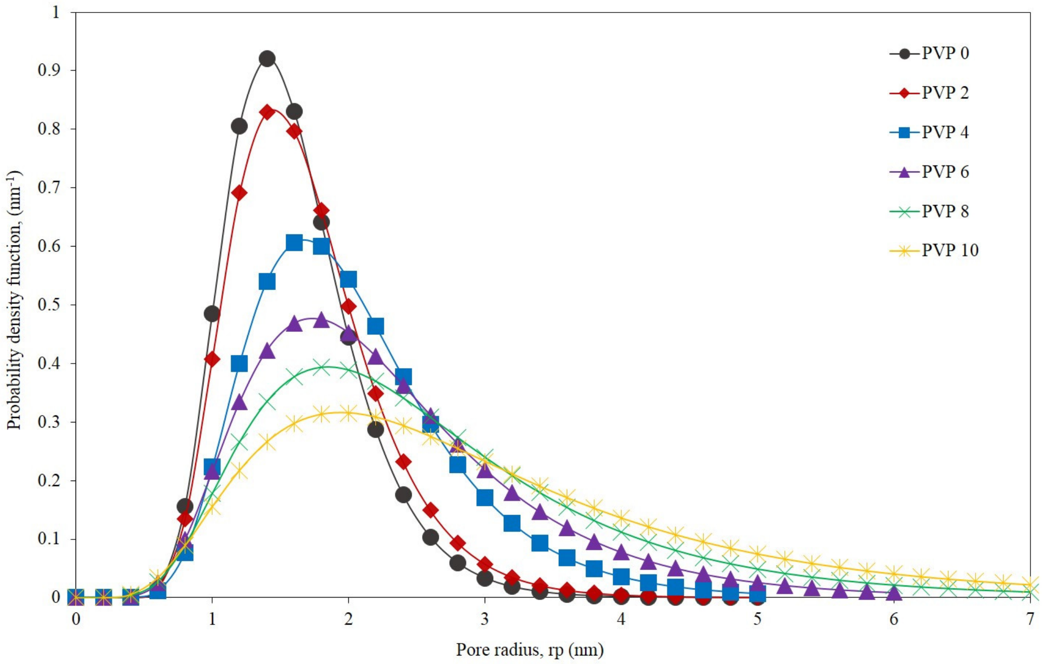

Fig. 2 Membranes pore size distribution (PSD) of narrow pores NF membranes

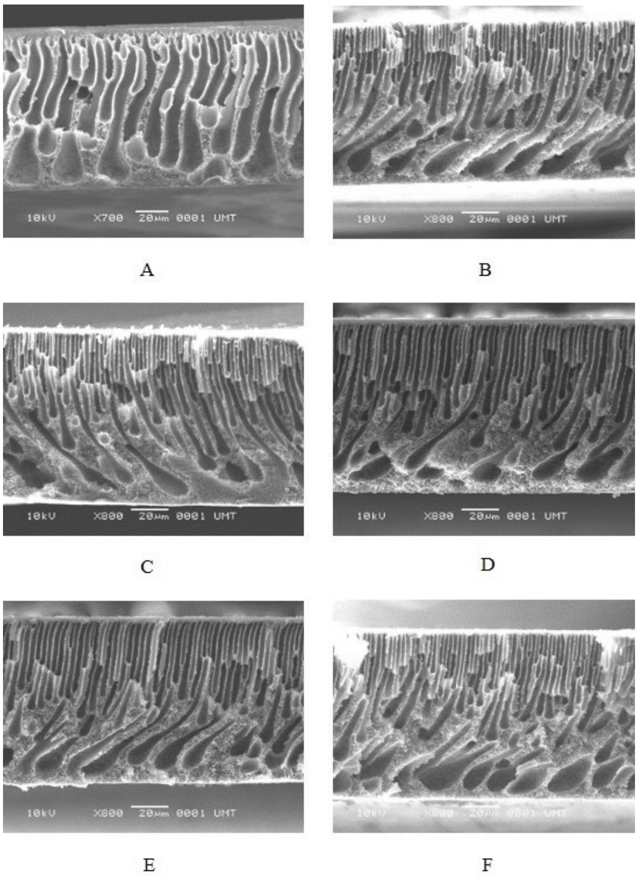

Fig. 3 Morphologies of narrow pore NF membranes (A = 0 wt%, B = 2 wt%, C = 4 wt%, D = 6 wt%, E = 8 wt%, F = 10 wt%)

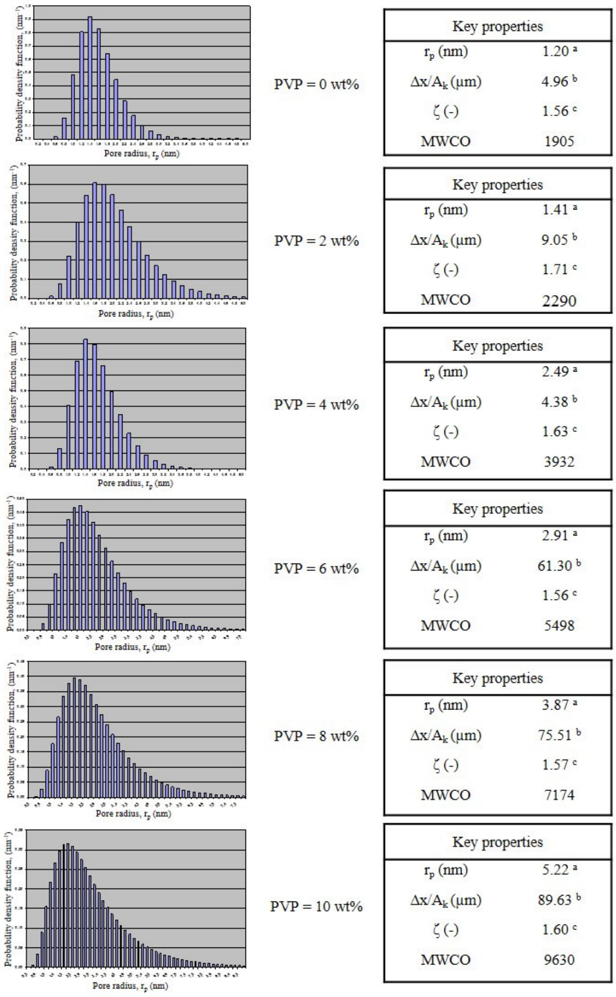

Fig. 4 PSD and properties of narrow pores asymmetric nanofiltration membranes ([a,b,c] are the modeling data from [22])

produced narrow pores and MWCO (1.14 nm and 2290 Da) led the fabricated membranes towards the highest salt rejection and flux of about 46.94% and 3.606×10^{-6} m^3/m^2s, respectively. Besides, the used of PVP additive produced the finest morphological structures and key properties as well as narrow pores distributions which are very practical for enhancement of nanofiltration separation capability.

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Nomenclatures

A_0	intercept
A_1	slope
c_b	salt concentration in bulk
c_p	salt concentration in permeate
c_w	salt concentration in wall
D_s	diffusivity in dilute solution (m^2/s)
F	Faraday constant (96487) (C/mol)
J_v	volume flux (m/s)
k	Boltzmann's constant, or mass transfer coefficient
M_w	molecular weight (g/mol)
r_p	pore radius (m)
r_s	Stokes radius of solute (m), or radius of solute (m or nm)
R	rejection, or gas constant (8.314) (J/mol^3 K)
R_{obs}	observation rejection
R_{real}	real rejection
T	temperature (K)
$\Delta X/A_k$	ratio of membrane thickness to membrane porosity

Greek letters

σ_g geometric standard deviation about the mean radius
σ_p geometric standard deviation
ζ zeta potential
μ solvent viscosity (water at 291.15 K is about 1.056 Ns/m^2)
μ_p mean pore size
μ_s geometric mean radius of solute

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